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water, and estimating the protoxide of iron with standard solution of bichromate of potash.

61·73 grns. of ore, dried at 212°, required 535 measures of standard solution of bichromate.

52·51, dried at 212°, required 450 measures of standard solution, whereof 1000 measures = 4·82 iron.

Determination of Phosphoric Acid.

No. 1. 61·55 grns. of ore, dry at 212°, gave $2MgO.PO_5$. 1·71
" 2. 42·78 „ „ „ . 1·27

The phosphoric acid was determined by the method proposed by A. Dick; viz.: by dissolving the ore in hydrochloric acid, filtering off insoluble matter, reducing the filtrate with sulphite of soda, and boiling off all free sulphurous acid, oxidizing a small portion of the solution with nitric acid, nearly neutralizing with ammonia, adding acetate of soda and boiling. All the phosphoric acid is then precipitated, together with a small amount of sesquioxide of iron, some of which goes down as basic acetate. The precipitate was collected and dissolved in hydrochloric acid; tartaric acid, ammonia, chloride of ammonium, and a magnesian salt were added; the liquid was allowed to stand two nights; and the precipitate was collected, filtered, and weighed as $2MgO.PO_5$.

Determination of Sulphur.

No. 1. 66·51 grns. of ore dry at 212°, gave $BaO.SO_3$. 0·92
„ 2. 46·28 „ „ „ . 0·84

The sulphur was determined by fusing the ore with a mixture of pure carbonate of soda and nitre in a gold crucible, dissolving in dilute acid, evaporating to dryness, and separating insoluble matter by redissolving in dilute hydrochloric acid, then precipitating by chloride of barium.

Determination of Carbonic Acid.

No. 1. 103·19 grns. of ore, dry at 212°, gave CO_2 . . 4·76
2. 65·24 „ „ „ . . 3·22

The carbonic acid was determined by dissolving the ore in a small flask provided with a safety funnel, and collecting the gas in potash-bulbs after drying it by passing through a chloride of calcium tube.

Organic Matter and Alkalies.

104·37 grns. of ore, dried at 212°, were dissolved in hydrochloric acid and silica, and the insoluble residue was separated, carefully detached from the filter, and treated in a platinum dish with hydrofluoric acid until all the silica was volatilized, and the clay was entirely decomposed; the partially dissolved mass was then treated with strong hydrochloric acid, and well boiled, and the organic matter left undissolved was collected on a tared filter and weighed . . . 0·63

The filtrates from the silica, and the filtrate from organic matter, were mixed together and precipitated by ammonia, and the alkalies were determined as already described for clays. Alkaline chlorides obtained . 0·48

In the analysis of iron ores, the author has entirely given up the use of potash; the sesquioxide of iron, alumina, and phosphoric acid are weighed together, as in analysis No. 2, and then the mixture is dissolved in hydrochloric acid; any silica it may contain is filtered off; the iron is determined by standard solution, and the sesquioxide thus obtained is deducted from the mixed precipitate; then, by calculation, the phosphoric acid contained in it is ascertained by a special determination made for this acid; this is also deducted, and the residue is alumina. Estimations by loss are generally objectionable, but a long experience has proved to me that the above method is the most reliable.

Titanium in Pig Iron.—This metal has only been detected satisfactorily on one occasion in a sample of very siliceous grey pig, containing $4\frac{1}{4}$ per cent. of silicon; it was found in the following manner:—A large quantity of the pig was dissolved in hydrochloric acid to test for metals; the insoluble silica was separated by filtration, and the filter treated with nitric and hydrochloric acids, again filtered, and the solution, on being evaporated to drive off nitric acid, was unintentionally allowed to go to dryness. On redissolving in hydrochloric acid, some insoluble residue was left, which was separated by filtration, and treated, after burning in a platinum crucible, with hydrofluoric and sulphuric acids—it was not silica: on fusing with bisulphate of potash, it gavethe distinctive and characteristic reactions of titanic acid. In testing pig iron for titanium, care must be taken, as the author has in many cases obtained precipitates in testing for titanic acid, which he

considered to be the acid, but on further examination found to be perphosphate of iron. In dissolving pig iron in acids, if there is much silica and phosphorus, some phosphide of iron is almost sure to be left with the silica; and this, after being treated with hydrofluoric and sulphuric acids, is left as a residue of perphosphate of iron, which was, in some cases, confounded with titanic acid, until a more intimate knowledge of its properties had been obtained.

Titanium in Iron Ores.—It is a mistake to suppose that titanic acid is left with the silica in the analysis of an iron ore, or that it is completely separated by evaporation to dryness; a considerable amount of titanic acid is dissolved by strong hydrochloric acid. In an iron ore containing from 20 to 30 per cent. of titanic acid, nearly the whole of the titanic acid was dissolved in the hydrochloric acid, and only a small amount obtained with the silica. The author hopes shortly to be able to lay before the Society some experiments made with rutile in the manufacture of steel, and also some details as to the presence of titanium in iron and steel: his present opinion is that it does not alloy to any considerable extent with iron.

XLIII.—*On Berberine—Contributions to its History and Revision of its Formula.*

By J. Dyson Perrins, F.C.S.

The objects of this paper are to announce some new sources for the alkaloid berberine, to describe several of its salts hitherto unnoticed, and to review the formula proposed by Fleitmann.

The chemical history of berberine is somewhat remarkable, and it will not be out of place here to refer briefly to it. The first notice of this body has hitherto been attributed to Buchner and Herberger, who discovered it in *Berberis vulgaris*, in 1835. They erroneously regarded it as a weak acid, rather than as a powerful organic base, and Buchner's formula has long been abandoned. I find however that Chevallier and Pelletan deserve honourable mention as being the first observers of berberine; they accurately described it under the name of Zanthopicrite in 1826.

More recently Fleitmann* published an account of "Berberine and some of its Salts," clearly establishing its basic character, and propounding a formula replacing that which had resulted from the previous labours of Buchner. Fleitmann's formula has obtained general acceptance,† varied however by Gerhardt, who, on theoretical grounds, proposed the addition of a single equivalent each, of hydrogen and oxygen. In addition to many of the *Berberideæ*, various other sources for this alkaloid, so remarkable for its beautiful yellow colour, have been discovered—by Boedeker‡ in *Cocculus palmatus*, the calumba root of pharmacy, belonging to the natural order, *Menispermaceæ;* by Stenhouse§ in *Cœlocline polycarpa*, natural order *Anonaceæ*, an African wood from Sierra Leone; by myself‖ in *Coscinium fenestratum*, natural order *Menispermaceæ*, a root from Ceylon; by myself¶ also in *Xanthorriza apiifolia*, natural order *Ranunculaceæ*, a North American plant; by Mahla** in *Hydrastis Canadensis*, another of the *Ranunculaceæ*, also a North American plant, common in the United States, the rhizome of which is used in American pharmacy.

Some time before the publication of Mahla's paper, I had noted the occurrence of berberine in *H. Canadensis;* indeed it was through that observation I was led to make the present inquiry.

I can recommend *H. Canadensis*, which may be readily obtained in this country, as an excellent and available source for berberine; it yields about four per cent. of the crude alkaloid.

In addition to the sources already named, I have now to announce the following new ones: it seems unnecessary to describe the methods employed to isolate the alkaloid—they were always founded upon its solubility in alcohol and the sparing solubility of the nitrate in solutions acidulated with nitric acid.

In the India Museum, there is a yellow dye-wood from Upper Assam, called by the native name *Woodunpar;* of this I obtained

* Chem. Gaz. 1847 vol. v. p. 129; Ann. Ch. Pharm. lix. 60.

† Except by *Kemp*, vide Chem. Gaz. v. 5, p. 209, who proposed a formula which has found no support; his platinum determinations agree with Fleitmann's and my own, but most unaccountably his carbon determinations of the platinum-salt are about two per cent. higher than those of any other chemist before or since.

‡ Chem. Gaz. vol. vi. 302.

§ Pharm. J. Trans. 1855, vol. xiv. p. 455.

‖ Phil. Mag. [4] iv. 99.

¶ Pharm. J. Trans. 1862, vol. iii. 567.

** Silliman's Journal, 1862, vol. xxxiii. p. 43.

a specimen through the courtesy of Dr. J. Forbes Watson; I find that berberine constitutes its yellow-colouring principle. I regret that I have been unable to ascertain the proper botanical name; from its structure it probably belongs to the order *Menispermaceæ*.

A woody root called *Raiz de São Joao*, or St. John's root, from Rio Grande, I believe twice imported into this country, and of which a specimen has been kindly given to me by Daniel Hanbury, Esq., F.L.S., &c., abounds in berberine; in this instance also I am unable to give the botanical designation. I gladly avail myself of this opportunity of expressing my sense of the kind assistance I have received from my friend Mr. Hanbury in the course of this inquiry. Amongst numerous rare specimens, this gentleman has favoured me with, is a yellow bark from the Botanical Museum at Kew, of which little appears to be known; it is simply named "*Pachnelo* tree—*yellow dye—Boyotà.*" This bark I find to be very rich in berberine, of which it yielded nearly seven per cent. of its weight. If further inquiry should show that pachnelo-trees are plentiful in New Grenada or other districts in South America, a most valuable source for berberine will be secured.

The next source for this alkaloid which I have to announce is one of considerable interest; it is the root of *Coptis Teeta* or *Mahmira*, a ranunculaceous plant of Hindostan and China, highly prized on account of its tonic properties, and known in the bazaars of India as *Mishmee bitter*. There is an historical notice of this root from the pen of the late Dr. Pereira.* He regards it as probable that *Coptis Teeta* is a remedy of great antiquity, in fact a classical medicine, used in ancient Greece and described by certain Greek and Arabian authors; in more recent times known in Europe under another name, but its origin not suspected; the first accurate notice of the root by any modern writer was given by Dr. Wallich, from whose account I quote:—"Mishme Teeta is the name by which the drug is designated among the Mishmees and Lamas in the mountainous regions bordering upon Upper Assam. The Chinese call it *Honglane*; among these three nations it is in great estimation and universal use as a powerful tonic and stomachic. Quantities are sent down to Assam in neat little baskets, with open meshes made of narrow slips of ratan or some

* Pharm. J. Trans., 1851, vol. xi. 294

such material, and measuring three to four inches in length by two and a half in breadth. Each basket contains about an ounce of small pieces of the root from one to three inches long; they are nearly cylindric, uneven, scabrous, more or less curved, of a greyish-brown colour, and varying in thickness from the size of a crow-quill to double that diameter. The root is perfectly dry and brittle; occasionally a few fibrillæ are issuing from one end; the inside is hard, somewhat cellular, the outside of a dingy, yellow colour. The taste is intensely and purely bitter, very lasting and with only a very slight aroma. On mastication, the root tinges the saliva yellow or gold-coloured, it possesses no smell whatever."

This account well describes a quantity of the root which I received from the East India Museum, through the kindness of Dr. J. Forbes Watson. I soon ascertained that the active principle of *Coptis Teeta* is berberine, in which the root abounds. I obtained from it eight and a half per cent., which is the largest amount yet met with, nor will it probably ever be surpassed. I did not obtain any other crystalline substance from this root.

Lastly, I have succeeded in establishing the fact that Zanthopicrite obtained from *Zanthoxylum Clava Herculis,* by Chevallier and Pelletan,* in 1826, is no other substance than berberine, and that consequently they must be considered as the first observers of this body. My friend, Mr. Hanbury, again assisted my inquiry, by furnishing me with some of the bark of *Z. clava Herculis,* according to Dr. Julius Martiny, a German pharmacologist of eminence, this bark is somewhat peculiar, from its highly laminated texture, splitting readily into thin plates like garden bast; this is noticed by the French authors, and altogether the careful description they give exactly applies to the bark which I have examined. The botanical synonyms are *Z. clava Herculis,* Linn.; *Z. Carolinianum,* Gaertner; and *Z. Caribæum,* Lamarck; it is quite necessary to particularize this, in order to prevent the confusion consequent upon the last-named botanist applying the specific term *Z. clava Herculis* to a tree which is totally distinct.

The French chemists do not appear to have attempted the ultimate analysis of their zanthopicrite, but they have carefully noted several of its properties and re-actions, not omitting the somewhat unusual deportment of this body with sulphide of

* Journ. de Chemie med., 1826, vol. ii. 314; Note sur le *Zanthoxylum des Caraïbes* ou *Clavalier des Antilles* par MM. Chevallier et Gabriel Pelletan. This bark is used in the West Indies as a febrifuge.

potassium. My own results have clearly proved the identity of zanthopicrite and berberine.

Z. clava Herculis belongs to the natural order *Rutaceæ*, and furnishes the first recorded example of berberine being a product of any plant of that order.

I now proceed to detail the numerical results I have obtained. It seems unnecessary to state in each case, from which plant I have prepared the salt for analysis; suffice it to say, that the whole of the sources now first announced are included.

It is not without some hesitation that I allow myself to question the conclusions of chemists of the eminence of Fleitmann, Boedeker, and others; but my own results are so accordant with each other, the number of analyses I have made, and the variety of combinations I have examined are so considerable, that I feel not only justified in proposing an alteration of the formula, but, indeed, compelled to do so. Perhaps, my hesitation is lessened by the recollection that, on a former occasion, I acquiesced in Fleitmann's formula, and even supposed that it was confirmed by my analysis of the hydrochlorate, and by a platinum determination; but later experience has shown me that the hydrochlorate is not suited for ultimate analysis, as by pretty long exposure to a temperature of 100°C., or thereabouts, it undergoes some decomposition, the colour changes permanently, and much of it becomes readily soluble in cold water, yielding a red solution; in these respects, it differs from the undried salt, thus proving that some alteration by heat has taken place. The pure alkaloid itself is equally unsuited for analysis, and for similar reasons, indeed I find it not easily prepared in a state of purity. With regard to the platinum determinations of some previous chemists, it is evident that impure products have been examined. I find that very many crystallizations are necessary before any of the salts of berberine can be pronounced pure. I must also state that the numerical results of Fleitmann agree with mine in many cases, and support the formula I propose rather than his own.

Fleitmann's formula is $C_{42}H_{18}NO_9$.* A glance at these numbers will suggest great doubts of their accuracy, the number of oxygen equivalents and the sum of those of hydrogen and nitrogen being indivisible by two; Gerhardt observed this, and proposed to represent berberine by $C_{42}H_{19}NO_{10}$? His alteration has

* C = 6. O = 8; for the sake of comparison, these values will be retained through this paper.

the effect of increasing the atomic weight, which my results point out as being already too high. The formula I propose is $C_{40}H_{17}NO_8$, which, with Gerhardt's, is equally free from theoretical objection, and I hope to show that it is fully borne out by abundant analytical proof.

As the platinum-salt possesses many advantages for determining the composition of the alkaloid, I have from time to time examined it; it may be prepared with ease in a pure state, in consequence of its great insolubility; like every other combination of berberine, it may be obtained in minute crystalline needles by precipitating a hot dilute solution of any berberine salt with bichloride of platinum. When collected, the precipitate should be washed with cold water, until the washings, upon the addition of iodide of potassium, give no evidence of the presence of platinum; it may then be dried at once in the water-oven without any fear of decomposition, and it burns without difficulty.

Analysis of *Chloroplatinate of Berberine*:—

No. 1.—4·451 grains, burned with lead-chromate, gave
7·250 „ carbonic acid, and
1·369 „ water.

No. 2.—6·604 grains gave
10·714 „ carbonic acid, and
2·033 „ water.

No. 3.—5·681 grains, burned with soda-lime for nitrogen determination, gave
1·127 „ platinum.

No. 4.—5·449 grains gave, on careful ignition,
·988 „ platinum.

No. 5.—2·733 grains gave
·679 „ platinum.

No. 6.—5·455 grains gave
·990 „ platinum.

No. 7.—3·879 grains gave
·705 „ platinum.

No. 8.—3·781 grains gave
·686 „ platinum.

No. 9.—3·350 grains gave
·610 „ platinum.

No. 10.—5·091 grains gave
·932 „ platinum.

No. 11.—4·310 grains gave
·790 „ platinum.

No. 12.—5·880 grains gave
1·075 „ platinum.

Percentage composition—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
C	44·42	44·24										
H	3·41	3·42										
N			2·80									
Pt.				18·13	18·19	18·14	18·17	18·14	18·20	18·31	18·33	18·28

leading to the formula $C_{40}H_{17}NO_8.HCl.PtCl_2$ as will be seen from the following comparison:—

	Calculated		Perrins. mean.	Fleitmann. mean.
40 equivs. carbon	240	44·35	44·33	44·39
18 „ hydrogen ..	18	3·33	3·41	3·50
1 equiv. nitrogen ..	14	2·59	2·80	
8 equivs. oxygen	64	11·83		
3 „ chlorine ..	106·5	19·68		
1 equiv. platinum ..	98·6	18·22	18·21	18·11
1 equiv. chloroplatinate of berberine	541·1	100·00		

It should be stated that every determination was from a different crystallization of the salt, often prepared at long intervals.

From this, one of the most precise methods known, it will be seen that not only my own results, but Fleitmann's also, point to the adoption of the proposed formula; that of the German chemist requiring but 17·53% of platinum, or less by 0·7%; and of carbon 44·83%, or more by 0·4%, a divergence from the foregoing results which appears to me, all but decisive on the point of its inaccuracy.

Chloroaurate of Berberine.

This combination was examined as possessing an advantage

even over the platinum-salt for the object in view, owing to the high combining weight of gold.

On adding terchloride of gold to the hydrochlorate or other salt of berberine, the double gold-salt immediately falls as an amorphous brown-coloured precipitate, quite insoluble in water; it is purified for analysis by washing with water, and dissolving in boiling dilute spirit, from which it crystallizes on cooling in chestnut-brown needles, which may be dried at 100°C. without decomposition, it burns without difficulty :—

No. 1.—8·209 grains gave, on combustion,
10·687 „ carbonic acid, and
2·004 „ water.

No. 2.—6·862 grains gave
8·932 „ carbonic acid, and
1·706 „ water.

No. 3.—5·600 grains gave, on ignition,
1·643 „ gold.

No. 4.—7·988 grains gave
2·317 „ gold.

No. 5.—7·950 grains gave
2·316 „ gold.

In 100 parts—

	1.	2.	3.	4.	5.
Carbon	35·50	35·50			
Hydrogen..	2·71	2·76			
Gold			29·34	29·00	29·13

corresponding to the formula

$$C_{40}H_{17}NO_8.HCl.AuCl_3,$$

as the following comparison will show :—

	Calculated.		Experiment.
40 equivs. carbon	240	35·57	35·50
18 „ hydrogen ..	18	2·67	2·74
1 equiv. nitrogen....	14	2·08	
8 equivs. oxygen	64	9·49	
4 „ chlorine....	142	21·05	
1 equiv. gold	196·6	29·14	29·16
1 equiv. double gold-salt	674·6	100·00	

Fleitmann does not appear to have examined this salt, but according to his formula, the amount of gold should be only 28·26%, or nearly one per cent. less.

The next combination to be described is interesting, as belonging to a class that I do not remember to have seen noticed before, viz., the double hyposulphites of silver and the alkaloids.

Hyposulphite of Berberine and Silver is precipitated in a yellow amorphous pulverulent form, when to a cold neutral solution of a salt of berberine is added hyposulphite of soda, saturated, ornearly so, with any silver-salt. The precipitant may be prepared by adding nitrate of silver to solution of hyposulphite of soda, so long as the precipitate first formed is redissolved; it must be filtered and used while fresh, as in time the silver is gradually deposited as sulphide.

The double berberine-salt is insoluble in water, but readily so in spirit, and in solution of hyposulphite of soda; it is decomposed by ebullition, with separation of sulphide of silver. To prepare the salt for analysis, I add the argentine solution to nitrate of berberine dissolved in weak spirit, while hot; the double salt crystallizes out on cooling in minute prisms of a pure lemon-yellow colour; they are readily washed with water, and the air-dried salt does not decompose or alter in colour at 100° C. Upon careful and prolonged ignition, nothing is left but perfectly white metallic silver :—

No. 1.—5·958 grains, burned with usual precautions, gave
9·381 „ carbonic acid, and
1·730 „ water.

No. 2.—6·553 grains gave
10·380 „ carbonic acid, and
1·910 „ water.

No. 3.—5·56 „ grains, burned with carbonate of soda and oxide of mercury, gave
4·646 „ sulphate of baryta.

No. 4.—6·625 grains gave, on ignition
1·290 „ silver.

No. 5.—5·997 grains gave
1·165 „ silver.

In 100 parts—

	1.	2.	3.	4.	5.
Carbon....	42·94	43·20			
Hydrogen..	3·22	3·24			
Sulphur ..			11·47		
Silver				19·47	19·42

leading to the formula

$$C_{40}H_{17}NO_8,HO.S_2O_2,AgO.S_2O_2,$$

as is shown by the following comparison :—

		Calculated.		Experiment.
40 equivs.	carbon	240	43·16	43·07
18 „	hydrogen ..	18	3·23	3·23
1 equiv.	nitrogen....	14	2·52	
14 equivs.	oxygen ...	112	20·16	
4 „	sulphur	64	11·51	11·47
1 equiv.	silver.....	108	19·42	19·45
1 equiv.	double silver salt	556	100·00	

Bichromate of Berberine.—This salt has been described by Fleitmann as an amorphous substance. I have to remark that it may be obtained in orange-yellow needles by adding bichromate of potassium to a boiling and very dilute solution of a salt of berberine—the crystals separate entirely on cooling. This salt is extremely insoluble in excess of the precipitant and in cold water, but it may be recrystallised from a large quantity of hot water. It burns readily, and the green oxide of chromium may thus be determined with exactitude. This salt agrees in constitution with the bichromates of ammonia, lepidine, chinoline, &c., in containing only one atom of water :—

No. 1.— 6·094 grains gave, on combustion,
11·964 „ carbonic acid, and
2·198 „ water.

No. 2.— 4·432 grains gave
8·747 „ carbonic acid, and
1·624 „ water.

No. 3.— 8·490 grains gave, on incineration,
1·480 „ sesquioxide of chromium.

No. 4.—10·149 grains gave
1·770 „ oxide of chromium.

In 100 parts—

	1.	2.	3.	4.
Carbon	53·54	53·87		
Hydrogen	4·00	4·07		
Oxide of chromium			17·43	17·44

agreeing with the formula*

$$C_{40}H_{17}NO_8HO,2CrO_3$$

as is shown by the following comparison :—

	Calculated.		Experiment.
40 equivs. carbon	240	53·86	53·71
18 „ hydrogen	18	4·04	4·04
1 equiv. nitrogen.....	14	3·14	
12 equivs. oxygen	96	21·55	
1 equiv. oxide of chromium. (Cr_2O_3)	77·6	17·41	17·43
1 equiv. bichromate of berberine	445·6	100·00	

Nitrate of Berberine.—This salt has been described by Fleitmann: it is so little soluble in slight excess of nitric acid, that it admits of repeated crystallizations without perceptible loss. It dissolves pretty readily in water, but separates most completely upon the addition of a few drops of dilute nitric acid. To insure its purity, I find it is necessary to crystallize repeatedly until the colour of the mother-liquor is no longer darkened by excess of ammonia, which may be considered as a proof that solutions of pure berberine do not assume a red colour upon the addition of an alkali; any change of colour is evidently due either to impurity or it points to some alteration in the alkaloid. Nitrate of berberine is to be preferred as the source from which to prepare every other combination; it may be subjected for any length of time to 100° C. without losing its fine yellow colour, having in this respect a great advantage over the hydrochlorate. For analysis, I finally crystallized it from hot water to get rid of every trace of free acid.

* Fleitmann's analysis of this salt does not agree very closely with mine, which is not surprising, as he did not obtain it in crystals, but examined an amorphous powder of difficult purification; his view of its constitution is unsatisfactory, and appears to be erroneous.

I found the nitrate admirably adapted for analysis, as the following concordant results will show :—

No. 1.—5·002 grains gave, on combustion,
11·032 „ carbonic acid, and
2·058 „ water.

No. 2.—5·213 grains gave
11·504 „ carbonic acid, and
2·149 „ water.

No. 3.—4·516 grains gave
9·970 „ carbonic acid, and
1·868 „ water.

No. 4.—4·046 grains gave
8·927 „ carbonic acid, and
1·673 „ water.

No. 5.—4·535 grains gave
10·014 „ carbonic acid, and
1·913 „ water.

In 100 parts—

	1.	2.	3.	4.	5.
Carbon	60·15	60.18	60·21	60·17	60·22
Hydrogen ..	4·57	4·58	4·57	4·59	4·68

corresponding with the formula

$$C_{40}H_{17}NO_8.HNO_6,$$

as is shown by the following comparison :—

		Calculated.		Experiment.	Fleitmann.*
40 equivs.	carbon.....	240	60·30	60·19	59·89
18 „	hydrogen.....	18	4·52	4·60	4·68
2 „	nitrogen	28	7·03		
14 „	oxygen.....	112	28·15		
1 equiv.	nitrate of berberine..	398	100·00		

Hydrobromate of Berberine may be prepared by adding bromide of potassium to solution of nitrate of berberine, acidulated with acetic acid. It instantly falls as a yellow precipitate soluble in pure

* Fleitmann's carbon determinations were 59·64 and 60·15 per cent.

water, but insoluble in excess of bromide of potassium; from its solution in hot water or spirit, it falls in yellow acicular crystals, which bear a temperature of 100° C. without decomposition, but assume a bright orange colour:—

No. 1.— 5·450 grains, on combustion, gave
11·505 „ carbonic acid, and
2·125 „ water.

No. 2.— 4·960 grains gave
10·360 „ carbonic acid, and
1·914 „ water.

No. 3.—13·308 grains gave
5·936 „ bromide of silver.

In 100 parts—

	1.	2.	3.
Carbon	57·57	57·66	
Hydrogen	4·33	4·34	
Bromine			19·00

corresponding with the formula

$$C_{40}H_{17}NO_8.HBr$$

as is here shown:—

	Calculated.		Experiment.
40 equivs. carbon	240	57·69	57·62
18 „ hydrogen ..	18	4·32	4·33
1 equiv. nitrogen ..	14	3·37	
8 equivs. oxygen	64	15·39	
1 equiv. bromine ..	80	19·23	19·00
	416	100·00	

The salt dried in vacuo lost 5·75 per cent. of water at a temperature of 100° C., which amount agrees pretty closely with three equivalents, and consequently it may be represented by

$$C_{40}H_{17}NO_8.HBr.3aq.$$

Hydriodate of Berberine.—Like other combinations of this alkaloid, the hydriodate occurs in the form of minute yellow acicular crystals: it is easily prepared in the same manner as the preceding salt, substituting, of course, iodide of potassium for the bromide; the hydriodate is extremely insoluble, whether in pure

water or in excess of the precipitant. It does not lose weight at 100° C. nor suffer any decomposition or change of colour.

Highly dilute solutions of berberine yield a precipitate on the addition of iodide of potassium. For analysis it is best prepared by precipitating a weak solution of nitrate of berberine in hot dilute spirit, with iodide of potassium. Crystals fall immediately: they may be washed upon a filter with water for some time without loss:—

No. 1.—5·905 grains gave, on combustion,
11·199 „ carbonic acid, and
2·094 „ water.

No. 2.—6·495 grains gave
12·329 „ carbonic acid and
2·304 „ water.

No. 3.—5·205 grains gave
2·602 „ iodide of silver.

No. 4.—7·005 grains gave
3·514 „ iodide of silver.

In 100 parts—

	1.	2.	3.	4.
Carbon	51·72	51·77		
Hydrogen ..	3·92	3·96		
Iodine.....			27·02	27·12

corresponding with the formula

$$C_{40}H_{17}NO_8.HI$$

as the following table shows:—

	Calculated.		Experiment.
40 equivs. carbon	240	51·83	51·75
18 „ hydrogen	18	3·88	3·94
1 equiv. nitrogen	14	3·03	
8 equivs. oxygen	64	13·83	
1 equiv. iodine	127	27·43	27·07
1 equiv. hydriodate of berberine	463	100·00	

Hydriodate of Biniodo-berberine, or Teriodide of Berberine?

This compound is formed when a slight excess of iodine is added

to solution of any berberine salt, either in water or spirit: in the latter solvent it dissolves on heating, and crystallizes in the form of transparent red-brown prisms, which are of extremely sparing solubility either in cold alcohol or in water; in the latter liquid they may be considered quite insoluble, as they do not impart any tinge of colour to it.

This compound is not a substitution-product; nitrate of silver rapidly removes all the iodine, with formation of nitrate of berberine. For analysis, the substance was dried at 100°C. and burned with chromate of lead and a pretty long column of reduced copper-turnings; this salt dried over oil of vitriol does not lose weight at 100 C.

No. 1.— 6·832 grains gave
8·405 „ carbonic acid, and
1·585 „ water.

No. 2.— 6·120 grains gave
7·502 „ carbonic acid, and
1·424 „ water.

No. 3.—10·877 grains ignited with pure lime gave
10·733 „ iodide of silver.

in 100 parts—

	1.	2.	3.
Carbon	33·55	33·43	
Hydrogen	2·57	2·58	
Iodine			53·36

corresponding with the formula

$$C_{40}H_{17}NO_8I_2HI$$

as is shown by the following comparison:—

	Calculated.		Experiment
40 equivs. carbon	240	33·47	33·49
18 „ hydrogen	18	2·51	2·57
1 equiv. nitrogen	14	1·95	
8 equivs. oxygen	64	8·93	
3 „ iodine	381	53·14	53·36
1 equiv. of hydriodate of biniodo-berberine ..	717	100·00	

I have retained the nomenclature adopted by Anderson for the teriodides of codeine and papaverine, with which this salt is evidently analogous; perhaps the name I suggest is the more correct, and I prefer it; but, as Anderson has previously remarked, the rational constitution of these substances is obscure.

I have now to describe a remarkable compound of Iodine with berberine, having certain analogies with the quinine-salt termed Herapathite. When dilute solution of iodine in iodide of potassium is added to solution of any salt of berberine in hot spirit, *carefully avoiding an excess of iodine,* the new substance speedily makes its appearance in the form of brilliant green spangles, which increase in quantity as the solution cools; they are invariably accompanied by crystals of hydriodate of berberine, or by the red salt last described, nor have I been able to devise any method of preparation by which this admixture can be wholly prevented. The formation of this new body is an excellent test for the presence of berberine; minute quantities may be detected by this reaction. Its occurrence seems to be determined whenever tincture of iodine containing hydriodic acid is added to solution of any salt of berberine in hot weak spirit, scrupulously avoiding excess of iodine; rapid agitation appears to promote its formation, and the presence of any impurity to interfere with it. Like Herapathite, it bears a strong resemblance to particles of the elytra of cantharides, and to murexide; under the microscope it is seen to consist of crystals of a variety of forms, but I believe all derived from a rhombic prism; the larger crystals are wholly opaque; many of the smaller ones however are sufficiently thin to allow of the passage of light, which assumes a red-brown hue, sometimes inclining to violet; but the light is perfectly polarized, in this respect also resembling Herapathite, with which its optical properties are obviously similar.

I obtained this compound with the smallest admixture of hydriodate, and in the largest crystals, by heating in a strong bottle, solution of berberine in alcohol of 90%, with addition of iodide of ethyl, to 100°C.; upon cooling, the bottle contains crystals of hydriodate of berberine, but if exposed to full sunshine for one or two hours, the crystals pass into the green salt now under notice. When the change appears to be complete, the bottle must be removed from the sunshine, or else the crystals will further pass into the red iodine-salt last described. Exposure to diffused daylight for some days may be substituted for sunshine;

but with every precaution, I have not been able to obtain the substance free from foreign crystals. It is not easy to see why this iodide of ethyl process succeeds better than others; probably the gradual development of free iodine is important. By this method I have obtained crystalline plates one-fifth of an inch in length by about half that breadth—of course, perfectly opaque. When removed from the solution and well washed with weak spirit, to remove adhering iodine, they have a blackish-green colour with a fine metallic lustre, yielding a nearly black powder, which does not decompose at 100°C.

I am inclined to believe that in composition this body is identical with the red salt, and differs from it only in molecular arrangement,—certainly it passes with the utmost facility into hydriodate of biniodo-berberine, and *vice versâ*. Nitrate of silver removes the iodine with the same ease, and with the same formation of nitrate of berberine.

A carbon and hydrogen determination yielded respectively 35·65 and 2·78 per cent., or numbers a little higher than they should have been, doubtless attributable to the presence of hydriodate of berberine. An iodine determination gave me less than the theoretical quantity, which was to be expected; one cogent reason why I believe the proper designation of these salts to be hydriodate of biniodo-berberine, rather than teriodide of berberine, is founded upon the observation that the green compound is not formed in the presence of any substance which decomposes hydriodic acid, e.g. nitrous acid; the presence of ordinary sweet spirit of nitre, which always contains free nitrous acid, entirely prevents its formation.

The foregoing analytical results will, I imagine, be considered as almost conclusive proof that the proposed formula for berberine is the true expression for that base; and consequently the previous belief that this alkaloid contains 42 equivalents of carbon must be abandoned.

Upon the chemical constitution of berberine, I have no new remark to offer, beyond the observation, that the action of iodide of ethyl results only in the formation of hydriodate. I did not obtain any ethylated compound; but the substitution-products of berberine well deserve careful study. Fleitmann has glanced at a sulphur-compound; I believe it will be found that more than one such exist; the same may be said with regard to nitric acid,

bromine, chlorine, &c. Fleitmann has noticed what may be termed the ultimate action of nitric acid; but there appear to be several intermediate products, the knowledge of which will doubtless reward future inquiry.

Berberine evidently occupies a position among the vegetal alkaloids, of great interest in a scientific point of view—a position far more prominent than has hitherto been assigned to it; if noticed at all in our Manuals, it is dismissed in half a dozen lines. From inquiries, which can be termed little more than superficial, its occurrence has been shown in numerous plants, belonging to no less than five of the great vegetal families—the natural orders of the botanist—nor can it be doubted that many other sources yet remain to be discovered; its geographical distribution, even in the present state of our knowledge, is all but universal; it is to be found in almost every country, certainly in every climate, and in these respects it claims precedence over all the other alkaloids.

As regards its usefulness to man, I believe its importance is not yet fully recognised. Though it has been long used as a fine yellow dye, more especially for animal tissues, its chief claims to usefulness do not reside in its application to the economic arts—doubtless its therapeutic effects merit much careful investigation. Natural instinct has pointed out its value for the alleviation of human suffering, to nations widely separated and enjoying different degrees of civilisation. The polished Greeks, the semi-barbarous nations of Hindostan and China, the North American Indians, and the natives of tropical Africa, have been all impressed with the medicinal value of berberine. In the West India Islands and in American pharmacy, its virtues have long been recognised, though derived from different plants, and veiled under erroneous names: certainly, it holds a place in European pharmacy, but one of little prominence; yet it seems to possess properties scarcely inferior to quinine itself. Various medical writers have insisted upon its advantages as a remedial agent; their arguments it would be out of place here to recapitulate; but I am persuaded that nature has not placed berberine in nearly every country without some adequate purpose; there are evidences that its value is becoming better understood amongst ourselves, and I confidently anticipate that ere long its reputation will be greatly increased.

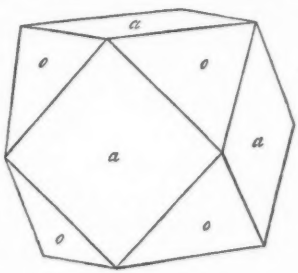
XLIV.—*On a Complex Cyanide of Iron, Copper, and Potassium.*

By William J. Wonfor,

Student in the Laboratory of the Museum of Irish Industry.

This complex cyanide crystallised in the form of reddish brown crystals, from a solution which had been employed in electro-plating, and was afterwards set aside and left undisturbed for several months; during that time the crystals made their appearance.

These crystals, for the measurement of which I am indebted to Professor W. H. Miller, of Cambridge, belong to the cubic system; they are combinations of the cube and octohedron. They resemble the annexed figure, the faces marked *a*, being the faces of the cube, and the faces marked *o*, those of the octohedron.



The angle between perpendiculars to any two adjacent faces *a*, is 90°.

The angle between perpendiculars to any two adjacent faces *o*, is 70° 30′.

The angle between perpendicular to any face *a* and an adjacent face *o*, is 54° 44′.

The following estimations give the amount of water lost in the water-bath:—

I.—1·936	grm.	lost	·0825	grm.	or	4·2613	per cent.
II.—0·9175	,,	,,	·0400	,,	,,	4·3590	,,
III.—0·5355	,,	,,	·0675	,,	,,	4·3310	,,
		Mean	-	-		4·3171	,,

For the estimation of the copper, iron, and potassium, the cyanide, dried at 212° F., was decomposed by Nordhausen sulphuric acid; the copper was first precipitated by sulphide of hydrogen; and the sulphide of copper was redissolved in nitric acid, precipitated by potash, and estimated as oxide in the usual way. The iron was peroxidised, then precipitated by ammonia, and

weighed as peroxide; whilst the potassium was weighed as sulphate of potash.

The analyses yielded the following results:—

I.—1·2972 grm. gave ·1966 grm. of Fe_2O_3 & ·6245 grm. of $KOSO_3$
II.—1·6431 „ „ ·2494 „ Fe_2O_3 & ·4718 „ CuO
III.—1·0735 „ „ ·3111 „ CuO & ·5168 „ $KOSO_3$

The nitrogen was estimated by Will and Varrentrapp's method, the substance employed being dried at 212° F.:—

I.—·888 grm. gave 2·447 grm. of NH_4Cl,Pl,Cl_2 = ·15345 of N.
II.—·7895 „ 2·180 „ „ = ·1365 „

The organic analyses were made with chromate of lead, the substance employed being dried at 212° F.:—

I.—·4836 grm. gave ·2617 grm. of CO_2 & ·0616 grms. HO.
II.—·6410 „ „ ·345 „ „ & ·0828 „ „

	I.	II.	Mean.
Iron	10·609	10·625	10·617
Potassium....	21·608	21·611	21·609
Copper	23·139	23·230	23·184
Nitrogen	17·284	17·289	17·287
Carbon	14·758	14·680	14·719
Hydrogen....	1·461	1·435	1·448
Oxygen.....	11·141	11·130	11·136
	100·000	100·000	100·000

These results may be expressed by the following calculations:—

		Calculated.
2Fe	56	10·113
3K	117	21·127
4Cu	126·8	22·896
7N	98	17·696
14C.....	84	15·168
8H	8	1·444
8O	64	11·556
	553·8	100·000

This salt lost in the water-bath 4·3171 per cent.; had it lost 4·73, it would correspond to 3 equivalents of water; this would give 11 as the total number of equivalents; but I am inclined to think, from a determination of the water which I made by combustion in an undried portion, that the true number of equivalents of water is 10. These calculations lead to the formula :—

$$(3KCy.2FeCy.2Cu_2Cy) + 10HO.$$

It is evidently the same substance that Bolley found deposited in a copper solution which had been employed in electro-plating; and subsequently Moldenhauer, seems to have formed it—if we may trust the incomplete analysis he has given—by boiling a solution of subcyanide of copper in a solution of ferrocyanide of potassium.

XLV.—*On the Formation of the Iodides of the Alcohol-radicles from Boghead Naphtha.*

By C. Greville Williams, F.R.S.

The possibility of passing from the bibasic to the monobasic radicles, by the addition of hydrogen to an oléfiant, through the medium of a hydracid, was first shown by M. Berthelot. The reaction with hydriodic acid is represented by the equation :—

$$C^nH^n + HI = C^nH^{n+1}I.$$

This reaction has been of the greatest service to me in pursuing my researches upon the hydrocarbons produced during the distillation of Boghead coal.

My first experiments were made to ascertain whether homologues of benzole and of marsh gas would, by dilution, prevent the action of the hydracids on the comparatively small quantity of the olefiant present. With hydrochloric acid this would appear to be the case. I then resorted successfully to fuming hydriodic acid, having a density between 1·8 and 1·9; a less concentrated acid has little action.

The following process appeared to yield the iodides more readily than any other yet tried. The naphtha, of a boiling point corresponding with that of the olefiant to be experimented on, was placed in a flask with a neck three or four feet long. About half the bulk of fuming hydriodic acid having been added, the mixture was cohobated for two or three hours. The neck was then cut off and replaced by a bent tube connected with a condensing apparatus. On applying a gentle heat, the hydrocarbons unacted on slowly distilled away. The more volatile portion having in this manner been removed, the distillation was carried on in a current of steam, until the distillate began to sink in water. The receiver was then changed and the product collected apart.

By proceeding in the manner described, I have obtained from Boghead naphtha the iodides of amyl, œnanthyl, capryl, and pelargonyl. It is evident, therefore, that Boghead naphtha may now be made to yield an almost infinite variety of products, some of them belonging to organic groups, which have, hitherto, almost escaped investigation.

The quantities of the iodides produced up to the present time, have been too small to allow direct analyses to be made: it became necessary, therefore, to employ some reaction by which a small quantity of iodide might be made to yield a comparatively large amount of a substance capable of being purified and analysed. For this purpose nothing appeared more suitable than the compound ammonias, because a very small amount of base could be made to yield a large quantity of platinum-salt.

With this intention the iodides were sealed up in strong tubes with a large excess of alcoholic ammonia, and heated to 100° C., for twelve hours. On opening the tubes and supersaturating the fluid with hydrochloric acid, a small quantity of oil remained undissolved, which was carefully removed. The soluble portion was then evaporated nearly to dryness, to expel the alcohol and traces of hydrocarbons. The solution distilled with excess of hydrate of potassium, yielded ammonia and an oily base. On adding a great excess of solid hydrate of potassium to the mixture, the alkaloid separated almost entirely, and, after distillation, was dissolved in hydrochloric acid and treated with an excess of chloride of platinum. The strength of the solution was so adjusted that no immediate precipitation took place. By exposing the dish containing the mixture, to a surface of sulphuric acid for a few hours, the salt was generally procured in fine crystals. In this manner

the platinum-salts of amylamine, œnanthylamine, caprylamine, and pelargonamine were prepared. The second and fourth of these bases are entirely new, and it is believed that none of them have ever before been procured from a homologue of olefiant gas.

I have not, as yet, been able to obtain any iodide of caproyl.

Platinum-salt of Amylamine.

Amylene is present in such small quantity in Boghead naphtha, that only a very minute portion of iodide of amyl could be obtained. I recognised the hydrochlorate at once by its peculiar fatty appearance; and the platinum-salt crystallised in superb scales, exactly resembling the salt which I had often had occasion to prepare by the ordinary processes.

The following numbers were obtained on analyses:—

I.—0·2135 gramme of platinum-salt of amylamine gave 0·0715 gramme of platinum.

II.—0·2004 gramme of platinum-salt of amylamine gave 0·0682 gramme of platinum.

Or, in per centages:—

Experiment.		Mean.	Theory.
I.	II.		
33·48	34·13	33·76	33·76

Platinum-salt of Œnanthylamine.

I have already shown the presence of œnanthylene in Boghead naphtha.* The quantity of iodide of œnanthyl formed, appears to be exceedingly small, and I was only able to obtain enough platinum-salt for one determination. It consisted of beautiful orange-coloured scales.

0·1186 gramme of platinum-salt of œnanthylamine gave 0·0366 gramme of platinum.

Experiment.	Theory.
30·86	30·79

Platinum-salt of Caprylamine.

The iodide of capryl appears to be formed more readily than its congeners. The crystals of the platinum-salt of the cor-

* Philosophical Transactions, 1858.

responding base consisted of beautiful golden scales, some of them a quarter of an inch in diameter. They were soluble in alcohol and ether; the salt was, therefore, washed with a little water and pressed between folds of filtering-paper. Several grammes were prepared with comparative ease.

The following numbers were obtained on analysis:—

I.—0·3432 grm. of platinum-salt of caprylamine gave 0·3616 grm. of carbonic acid, and 0·1906 grm. of water.
II.—0·2195 grm. of platinum-salt of caprylamine gave 0·0645 grm. of platinum
III.—0·2084 „ „ 0·0614 „
IV.—0·2028 „ „ 0·0596 „
V.—0·2066 „ „ 0·0616 „

	I.	II.	III.	IV.	V.	Mean.	Calculation.		
Carbon	28·73					28·73	C^{16}	96	28·62
Hydrogen	6·17					6·17	H^{20}	20	5·96
Nitrogen	. . .					. . .	N	14	4·17
Chlorine	. . .					. . .	Cl^3	106·5	31·74
Platinum	. . .	29·38	29·46	29·39	29·81	29·51	Pt	99	29·51
								335·5	100·00

The first and fourth analyses were made on the same specimen; the second, third, and fifth upon distinct preparations in each case.

Platinum-salt of Pelargonamine.

The iodide of pelargonyl was formed from Boghead naphtha in sufficient quantity to enable me to attain the hitherto unknown volatile alkaloid, pelargonamine. The crystals of the platinum-salt, although of a rich golden-yellow, were less beautiful than the others, and on drying at 100° C. caked slightly together. They did not, however, become in the least discoloured. The annexed numbers give the results of the analyses—

I.—0·3978 grm. of platinum-salt of pelargonamine gave 0·4474 grm. of carbonic acid, and 0·2304 grm. of water.
II.—0·1184 grm. of platinum-salt of pelargonamine gave 0·0340 grm. of platinum
III.—0·2132 „ „ 0·0604 „
IV.—0·2364 „ „ 0 0678 „

	I.	II.	III.	IV.	Mean.	Calculation.		
Carbon	30·70				30·70	C^{18}	108	30·90
Hydrogen	6·44				6·44	H^{22}	22	6·30
Nitrogen	. . .				. . .	N	14	4·01
Chlorine	. . .				. . .	Cl^3	106·5	30·47
Platinum	. . .	28·71	28·33	28·68	28·57	Pt	99	28·32
							349·5	100·00

Each platinum-determination was made on a different specimen. I hope, eventually, to submit to the Society several more substances obtained from Boghead naphtha by the agency of hydriodic acid. It is evident that several of the true radicles may now be prepared by acting on the above iodides with sodium.

XLVI.—*On a New Series of Organic Compounds containing Boron.*

By Dr. E. Frankland, F.R.S.

[From the Philosophical Transactions for 186?.]

(Abstract.)

The substitution of a compound organic radicle for an elementary constituent in inorganic compounds has proved itself to be one of the most important and fertile fields of modern chemical investigation. The application of this species of substitution to the inorganic compounds of metals has called into existence an entirely new and extensive family of organic substances—the organometallic compounds—bodies never met with in nature, distinguished by well-marked affinities, and capable in some instances of effecting, in their turn, numerous substitutions of a like character. The realization of a similar substitution in the case of certain inorganic compounds of nitrogen and phosphorus, has, in the hands of Hofmann, not only enriched the science with a host of new and interesting compounds, but has also brought our knowledge of the organic bases to a degree of completeness, which cannot be rivalled in any other class of organic compounds. Lastly,

attempts have not been wanting to extend these reactions to the oxygen-compounds of the metalloids; and although this portion of the field presents difficulties of a somewhat more formidable character, yet these attempts have not unfrequently been attended with success. Thus nitric oxide has been transformed into dinitroethylic and dinitromethylic acids;* sulphurous anhydride into ethylodithionic and methylotrithionic acids;† and carbonic anhydride into propionic and acetic acids.‡

The last-named reaction, confirming, as it did, the view previously expressed by Kolbe and myself,§ that organic compounds in general are nothing more than substitutions of this nature effected in carbonic oxide, in carbonic acid, and possibly in other inorganic compounds of carbon, naturally awakened a desire to extend this inquiry to the oxygen-compounds of boron and silicon, which are usually regarded as possessing certain important analogies with carbonic anhydride. With this end in view, boracic ether was submitted to the action of zincethyl by Mr. Duppa and myself. We found that the whole of the oxygen in boracic acid became replaced by ethyl, and in a short communication to the Royal Society,‖ we described some of the properties of the remarkable body, boric ethide, thus formed. In the further study of this substance, and the extension of the research to the homologous methyl-compound, I much regret having been deprived of the co-operation of my friend and fellow-labourer, who had rendered me such valuable assistance at the commencement of the investigation, but who was reluctantly compelled to abandon its further prosecution.

The first attempt to replace oxygen by ethyl in boracic anhydride was made by exposing the latter in a finely pulverized condition to the action of zincethyl at various temperatures, but it was found that the zincethyl was utterly powerless to effect the desired substitution; neither did the anhydrous acid yield in the slightest degree to Wanklyn's compound of sodiumethyl and zincethyl, although it was digested and heated with it for several days. There could scarcely be a doubt that the intractability of

* Philosophical Transactions for 1857, p. 59.

† Journal of Chemical Society, vol. x, p. 55, and p. 243.

‡ Ibid. vol. xi, p. 103; and Proceedings of the Royal Society, vol. x, p. 4.

§ Ann. Ch. Pharm. ci, 257. Proceedings of the Royal Institution of Great Britain for 1858.

‖ Proceedings of the Royal Society, vol. x, p. 568.

the anhydride was due in great measure to its total insolubility in the surrounding liquid, and therefore, in order to place it under conditions more favourable for the action of the organo-metallic body, it was converted into boracic ether.

The ether was prepared by Rose's process,* which consists in distilling an intimate mixture of sulphovinate of potash and dried borax. The best proportions were found to be two parts by weight of borax, and three parts of the sulphovinate; but the yield of ether was very small, the greater part of the product consisting of alcohol. The removal of the latter by rectification, as recommended by Rose, involved the loss of much ether; recourse was therefore had to chloride of calcium for its abstraction, a method which gave very satisfactory results, the product of pure ether being more than doubled. The following is a sketch of the process finally adopted:—About 3 lbs. of the mixed borax and sulphovinate of potash were put into an ordinary Papin's digester, which was placed in a sand-bath and exposed to a very gradually increasing heat so long as volatile products came over. The crude distillate obtained from several such operations was then treated with about one-fourth of its weight of fused chloride of calcium, and agitated until the latter was dissolved. The liquid now separated into two layers, a lower one consisting of an alcoholic solution of chloride of calcium, and an upper one containing nearly all the boracic ether, which retained only a small proportion of alcohol in solution. The upper layer was decanted and submitted to distillation. It began to boil at about 85° C., but the thermometer soon rose to 118° C., between which temperature and 125° C. the greater part of the remaining liquid passed over and was reserved for the purposes of the investigation. A thick oily liquid remained in the retort, and appeared to consist of boracic acid united with a smaller proportion of oxide of ethyl.

On adding zincethyl to the boracic ether thus prepared, a considerable elevation of temperature gradually occurred, whilst at the same time a most penetrating and peculiar odour was developed, due apparently to the vapour of some volatile body, which not unfrequently burst into flame when the cork was removed from the flask in which the reaction took place. Some preliminary experiments showed that this volatile body could be distilled unchanged from the mixture, and that it was neither miscible with, nor apparently decomposed by, water. It was also

* Pogg. Ann. xcviii, 245.

spontaneously inflammable, and the beautiful green flame with which it burnt demonstrated the presence of boron as one of its constituents.

In order to prepare this body in sufficient quantity, several ounces of boracic ether were placed in a capacious flask closed by a doubly perforated cork. Through one of these perforations passed a thermometer, and through the other a short glass tube, one-fourth of an inch in diameter, and open at both ends: the bulb of the thermometer dipped into the boracic ether. Successive quantities of pure zincethyl were introduced through the short glass tube by means of a pipette, the elevation of temperature after each addition being allowed to subside before the next portion was added. The failure of a further addition of zincethyl to produce any rise of temperature was regarded as evidence of the completion of the reaction, which was not attained until a comparatively very large amount of zincethyl had been added.

The liquid in the flask was now submitted to distillation in an oil-bath. It began to boil at 94° C., and between this temperature and 140° C., a considerable quantity of a colourless liquid distilled over. The distillation then suddenly stopped, and, to avoid secondary products of decomposition by the application of a greater heat, the operation was interrupted. On cooling, the materials remaining in the flask solidified to a mass of large crystals of ethylate of zinc and zincethyl. On rectification, the distillate began to boil at 70° C., but the thermometer rapidly rose to 95°, at which temperature the last two-thirds of the liquid passed over and were received apart. The product thus collected exhibited a constant boiling-point on re-distillation.

The combustion with oxide of copper of this liquid and the remaining boron-compounds described in this paper, presented some difficulties, owing partly to the volatility of boracic acid in aqueous vapour, and partly to the tendency of that acid when fused, to encase particles of carbon and prevent their oxidation. Fortunately the errors thus introduced were not so considerable as to throw any doubts upon the analytical results, although in many cases the excess in the percentage of hydrogen and the deficiency in that of carbon are somewhat greater than usual. To estimate the boron in the liquid obtained as above described, advantage was taken of the complete decomposition of the compound when heated to 100° with concentrated nitric acid in sealed tubes. The whole of the boron was in this way converted into

boracic acid; but the latter could not be determined by the direct evaporation of the nitric acid solution, the loss of boracic acid amounting in such an operation to 15 or 20 per cent. of the whole amount. None of the known processes for estimating this acid appeared to be eligible in the present instance, and it therefore became necessary to seek for a new one. After the trial of various methods with but indifferent success, it was found that the evaporation of the acid solution of boracic acid with a known weight of magnesia in excess, the residue being then ignited, presented a process which, although far from rigidly accurate, could not, in the case of the boron-compound to be analysed, diminish the amount of boron to a greater extent than about 0·2 per cent.

The analytical numbers agree with the formula

$$B\begin{cases}C_4H_5\\C_4H_5\\C_4H_5,\end{cases}$$

as shown by the following table:—

	Calculated.		Mean of analyses.
C_{12} . .	72	73·55	73·15
H_{15} . .	15	15·42	15·61
B . .	10·9	11·03	11·08
	97·9	100·00	99·84

The new body may be conveniently termed *boric ethide*. It is evidently formed by the replacement of the three atoms of oxygen in boracic acid by three atoms of ethyl, according to the following equation:—

$$\underbrace{2B\begin{cases}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{cases}}_{\text{Boracic ether.}} + \underbrace{3Zn_2\begin{cases}C_4H_5\\C_4H_5\end{cases}}_{\text{Zincethyl.}} = \underbrace{2B\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\end{cases}}_{\text{Boric ethide.}} + \underbrace{6\left\{\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}}_{\text{Ethylate of zinc.}} O_2.$$

The ethylate of zinc thus produced combines with zincethyl to form the crystalline compound above alluded to. Hence the very large amount of zincethyl which was found necessary to complete the reaction.

Boric ethide possesses the following properties:—It is a colourless mobile liquid of a pungent odour; its vapour is very irritating to the mucous membrane, and provokes a copious flow of tears. The specific gravity of boric ethide at 23° C. is 0·6961; it boils at 95° C. A determination of the specific gravity of its vapour by Gay-Lussac's method, gave the number 3·4006, which agrees very closely with that calculated upon the supposition that boric ethide is volumetrically composed like terchloride of boron, as is seen from the following calculation:—

1 vol. Boron vapour	·75319
3 vols. Ethyl	6·0117
The 4 vols. condensed to 2 vols. .	2)6·76489
	3·38244

The density of boric ethide vapour increases considerably as the temperature approaches the boiling-point; thus a determination made at 132° gave the number 3·5979, whilst a second showed the specific gravity of the vapour at 101°·6 to be no less than 3·757.

Boric ethide is insoluble in water, and is very slowly decomposed by prolonged contact with it. Iodine has scarcely any action upon it even at 100° C. It floats upon concentrated nitric acid for several minutes without change; but suddenly a violent reaction takes place, and crystals of boracic acid separate. When boric ethide vapour comes in contact with air, it produces slight bluish-white fumes, which in the dark are seen to proceed from a lambent blue flame. The liquid is spontaneously inflammable in air, burning with a beautiful green and somewhat fuliginous flame. In contact with pure oxygen it explodes. Excluded from the air, boric ethide is quite a stable body; a quantity of it kept in a sealed tube for two years exhibited, on examination, no evidence of any alteration.

When boric ethide is heated to 99° C. with strong hydrochloric acid over mercury, a considerable quantity of hydride of ethyl is slowly evolved, the reaction being

$$B\begin{Bmatrix}C_4H_5\\C_4H_5\\C_4H_5\end{Bmatrix} + HCl = B\begin{Bmatrix}C_4H_5\\C_4H_5\\Cl\end{Bmatrix} + \begin{matrix}C_4H_5\\H\end{matrix}\}$$

When boric ethide is heated with water to 99° C. for several hours, it also appears to suffer an analogous decomposition, although with extreme slowness; even with hydrochloric acid, the action is so tedious, that I have not been able to prepare a sufficient quantity of boric chlorodiethide ($B(C_4H_5)_2Cl$) to examine its properties. In the cold, a strong solution of hydrofluoric acid has no action upon boric ethide, which also suffers scarcely any change by being heated to 99° C. for four hours with concentrated sulphuric acid. Gently heated for fourteen days with sodium in a sealed tube, boric ethide underwent no visible change.

Ammonia-Boric Ethide.

If a few drops of boric ethide be passed up into a dry eudiometer filled with mercury, and dry ammoniacal gas be then admitted into the same tube, each bubble of gas collapses with a shock, like that produced by a bubble of steam projected into cold water. A large quantity of ammonia is thus absorbed by boric ethide with extreme energy. To prepare the compound thus formed in larger quantity, several grammes of boric ethide were placed in a small flask filled with nitrogen and surrounded with ice: a current of dry ammoniacal gas was now passed into the flask as long as it was absorbed; finally, the product thus obtained was warmed to expel excess of ammonia, and then exposed *in vacuo* over sulphuric acid for twenty-four hours. It did not crystallize, and and could not be distilled, except *in vacuo*, without decomposition. Submitted to analysis, it yielded 61·43 per cent. of carbon and 15·43 per cent. of hydrogen. The formula

$$NH_3.B(C_4H_5)_3$$

requires 62·66 per cent. of carbon and 15·66 per cent. of hydrogen. The unavoidable slight oxidation of the boric ethide during the necessary manipulations affords a sufficient explanation of the deficiency in the amounts of carbon and hydrogen exhibited by the analysis. I should, however, have made renewed attempts to obtain this body in a state of greater purity, had not the investigation of the corresponding crystalline methyl-compound described below, left no doubt that the formula above given expresses the composition of ammonia-boric ethide.

Ammonia-boric ethide is a somewhat oily liquid, possessing an aromatic odour and an alkaline reaction. Carbonic acid has no

action upon it, even in presence of water, but other acids decompose it instantly and liberate boric ethide. When it is exposed to a measured quantity of atmospheric air, there is scarcely any perceptible absorption of oxygen, even after the lapse of several hours.

Boric Dioxyethide.

When boric ethide is placed in a flask and allowed to oxidise gradually, first in dry air and finally in dry oxygen, it forms a colourless liquid, which boils at 125° C., but cannot be distilled under atmospheric pressure without partial decomposition. At the ordinary temperature, this product of oxidation evaporates without residue in a stream of dry carbonic acid. It can be distilled *in vacuo* without decomposition, and a portion so rectified yielded on analysis results agreeing with the formula

$$B(C_4H_5)_3O_4.$$

I regard this liquid as a compound of vinic ether, with a body having the formula

$$B\begin{cases} C_4H_5 \\ O \\ O \end{cases}$$

and derived from boracic acid by the substitution of one equivalent of ethyl for one of oxygen. For this body the name *boric dioxyethide* is appropriate, whilst its ethereal compound may be conveniently termed diethylate of boric dioxyethide. The formula of the latter will therefore be

$$B\begin{cases} C_4H_5 \\ O \\ O \end{cases} + \left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\} O_2, \text{ or } B\begin{cases} C_4H_5 \\ C_4H_5O_2 \\ C_4H_5O_2. \end{cases}$$

The formation of diethylate of boric dioxyethide from boric ethide may be thus represented :—

$$B\begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{cases} + O_4 = B\begin{cases} C_4H_5 \\ C_4H_5O_2 \\ C_4H_5O_2. \end{cases}$$

This view of the constitution and mode of formation of the oxidised product is supported by its behaviour with water; for when diethylate of boric dioxyethide is placed in contact with

water, it is instantly decomposed, alcohol and *dihydrate of boric dioxyethide* being formed, according to the following equation :—

$$B\begin{Bmatrix}C_4H_5\\C_4H_5O_2\\C_4H_5O_2\end{Bmatrix} + 2\begin{Bmatrix}H\\H\end{Bmatrix}O_2 = B\begin{Bmatrix}C_4H_5\\HO_2\\HO_2\end{Bmatrix} + 2\begin{Bmatrix}C_4H_5\\H\end{Bmatrix}O_2.$$

Diethylate of boric dioxyethide. Dihydrate of boric dioxyethide.

Dihydrate of boric dioxyethide may be conveniently prepared in a state of purity by agitating its aqueous solution with ether, which dissolves the boric compound. The ethereal solution must then be decanted, and on evaporation at common temperatures in a stream of dry carbonic acid, the new compound is left behind as a white and very volatile crystalline mass. The latter was sublimed at a gentle heat in a current of dry carbonic acid, and was made to condense in weighed tubes for analysis.

Dihydrate of boric dioxyethide is a colourless, volatile, crystalline body, very soluble in water, alcohol, and ether. It possesses an agreeable ethereal odour, and a most intensely sweet taste. Exposed to the air, it evaporates at ordinary temperatures, undergoing at the same time partial decomposition, and invariably leaving a slight residue of boracic acid. It may be sublimed without change at about 40° C. in a current of dry carbonic acid, and then condenses in magnificent crystalline plates resembling naphthaline. It fuses at a gentle heat, and at a higher temperature boils with partial decomposition. Its vapour tastes intensely sweet.

Boric dioxyethide might be regarded as the anhydride of a bibasic acid : the diethylate of boric dioxyethide would then be the ether of this acid, whilst the volatile crystalline body just described would be the hydrated acid itself. The latter does in fact redden litmus paper, but in other respects its acid qualities are very obscure, and I have not been able to form definite salts with it. It therefore scarcely possesses a valid claim to a place amongst the acids.

Considering boric ethide to be formed by the substitution of the ethyl in zincethyl for the oxygen in boracic acid, Mr. Duppa and myself expressed the reaction as follows :—

$$\underbrace{2B\begin{Bmatrix}C_4H_5O_2\\C_4H_5O_5\\C_4H_5O_2\end{Bmatrix}}_{\text{Boracic ether.}} + \underbrace{3Zn_2\begin{Bmatrix}C_4H_5\\C_4H_5\end{Bmatrix}}_{\text{Zincethyl.}} = \underbrace{2B\begin{Bmatrix}C_4H_5\\C_4H_5\\C_4H_5\end{Bmatrix}}_{\text{Boric ethide.}} + \underbrace{6\begin{Bmatrix}C_4H_5\\Zn\end{Bmatrix}O_2}_{\text{Ethylate of zinc.}}$$

Another, but less probable, view of the change presents itself in the supposition that the three atoms of ethyl in boric ethide were already present in the boracic ether, the action of the zinc-ethyl being simply to remove the whole of the oxygen from the boracic ether. Kekulé* has in fact adopted this latter view of the reaction.

So long as the organic radicle of the zinc-compound and that of the boracic ether are identical, it is impossible to prove whether the three individual atoms of ethyl in boric ethide were originally present in the boracic ether, or have been derived from the zinc-ethyl. Indicating by an asterisk the atoms of ethyl which finally become part of the boric ethide, it is impossible to prove conclusively whether the reaction takes place according to the first or the second of the following equations:—

$$(1)\quad 2B\begin{Bmatrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{Bmatrix} + 3Zn_2\begin{Bmatrix}C_4H_5*\\C_4H_5*\end{Bmatrix} = 2B\begin{Bmatrix}C_4H_5*\\C_4H_5*\\C_4H_5*\end{Bmatrix} + 6\begin{Bmatrix}C_4H_5\\Zn\end{Bmatrix}O_2.$$

$$(2)\quad 2B\begin{Bmatrix}C_4H_5*O_2\\C_4H_5*O_2\\C_4H_5*O_2\end{Bmatrix} + 3Zn_2\begin{Bmatrix}C_4H_5\\C_4H_5\end{Bmatrix} = 2B\begin{Bmatrix}C_4H_5*\\C_4H_5*\\C_4H_5*\end{Bmatrix} + 6\begin{Bmatrix}C_4H_5\\Zn\end{Bmatrix}O_2.$$

Although we cannot thus label, as it were, the atoms taking part in the reaction, we can unerringly trace the movements of the alcohol-radicles, if we secure their identification by varying their composition in the two compounds used in the process. The study of the action of zincmethyl upon boracic ether would obviously decide between these views. If boric ethide were produced from these materials, Kekule's hypothesis would be established; but if, on the other hand, boric methide were the result of the reaction, then the correctness of the view originally taken by Mr. Duppa and myself would be proved to be correct. The following are the results obtained in pursuing this inquiry:

* Lehrbuch der org. Chemie, p. 489.

Boric Methide.

When a strong ethereal solution of zincmethyl is added to boracic ether, an elevation of temperature to the extent of 8° or 10° C. is observed, whilst at the same time a most intensely pungent odour is developed; this odour, although it resembles that of boric ethide, is far more powerful, and more persistently irritating to the mucous membrane. A slow evolution of a spontaneously inflammable gas, burning with a splendid green flame, was also noticed; and this evolution of gas became more rapid when the warmth of the hand was applied to the flask containing the ingredients. Preliminary experiments proved that this gas was nearly insoluble in water, but almost completely soluble in alcohol, the residue remaining undissolved being marsh-gas derived from the action of the alcohol upon traces of zincmethyl vapour with which the gas was contaminated. The gas was not condensed by a freezing mixture of ice and salt. It was, with the exception of a small percentage of marsh-gas, instantaneously dissolved by solution of ammonia, which yielded the gas again unchanged when neutralized by an acid. Concentrated sulphuric acid was without action upon the gas.

These data led to the following plan for collecting the gas in a state of purity. About two ounces of boracic ether were mixed in a small flask with rather more than their own bulk of an ethereal solution of zincmethyl, of such strength as to be spontaneously inflammable in a high degree. The flask, loosely corked, was placed in ice-cold water, and allowed to stand for a couple of hours until the reaction was complete: it was then furnished with a bent tube passing through a cork, and designed to conduct the gas into a second flask placed in a freezing mixture of ice and salt; from this flask the gas passed into a third containing about half an ounce of strong solution of ammonia. The air in the whole of the apparatus was now displaced by nitrogen, and the flask containing the boracic ether and zincmethyl removed from the ice-cold water. A slow evolution of gas immediately commenced, and was kept up at a convenient speed by plunging the generating flask into cold water, to which heat was very slowly applied. The gas, in passing through the freezing mixture, deposited nearly the whole of the ether and zincmethyl

vapour with which it was contaminated; and on reaching the solution of ammonia, the boron-compound was instantaneously absorbed, whilst other gases, if present, passed through the ammonia unacted upon, and escaped into the atmosphere. The solution of ammonia soon became covered with a stratum of a lighter liquid, which increased in quantity until the stream of gas ceased to pass through. The ammonia-flask was now disconnected with the rest of the apparatus, and reserved for the next operation. The residue in the generating flask solidified to a crystalline mass on cooling.

It now only remained to disengage the gaseous boron-compound from its combination with ammonia. For this purpose the ammonia-flask was fitted with a funnel-tube terminating beneath the surface of the liquid, and a gas-delivery tube, the latter leading to a Liebig's potash-apparatus charged with concentrated sulphuric acid; finally, the opposite extremity of the latter apparatus was connected with a mercurial gas-holder. To prevent dangerous explosions, on the elimination of the spontaneously inflammable gas from its ammonia-compound, the whole of the air-spaces of the apparatus were filled with nitrogen. Everything being thus prepared, dilute sulphuric acid was gradually poured into the ammonia-flask through the funnel-tube, the contents of the flask being frequently agitated. No gas was evolved until the excess of ammonia was saturated; then, however, it was given off abundantly, and the addition of a few drops of dilute sulphuric acid, from time to time, through the funnel-tube, served to keep up a convenient current. The gas was allowed to pass freely through the depressed mercurial gas-holder until a sample of it proved, by its perfect solution in ammonia, that all nitrogen had been swept from the apparatus. The exit-tube of the gas-holder was now closed, and the gas collected in sufficient quantity for subsequent experiments.

The following determinations, together with the analysis of its ammonia-compound, prove that this gas is *boric methide*, and that its formula is

$$B\begin{cases}C_2H_3\\C_2H_3\\C_2H_3.\end{cases}$$

An indefinite quantity of the gas was cautiously led over ignited oxide of copper, the carbonic acid and water produced

being collected and weighed in the ordinary manner. 0·5875 grm. of carbonic acid and 0·3664 grm. of water were obtained. These numbers show that the atomic relation of carbon to hydrogen is as 2 : 3.

A determination of the specific gravity of the gas gave the number 1·9108—coinciding closely with the calculated specific gravity of boric methide, which contains 1 volume of boron vapour and 3 volumes of methyl, the four volumes being condensed to two.

1 vol. boron vapour . . .	·75319
3 vols. methyl	3·10956
	2)3·86275
	1·93137

Boric methide is produced from boracic ether and zincmethyl by the following reaction :—

$$2B\underbrace{\begin{Bmatrix}C_4H_5O_2\\C_4H_5O_2\\C_4H_5O_2\end{Bmatrix}}_{\text{Boracic ether.}} + 2Zn_2\underbrace{\begin{Bmatrix}C_2H_3\\C_2H_3\end{Bmatrix}}_{\text{Zincmethyl.}} = 2B\underbrace{\begin{Bmatrix}C_2H_3\\C_2H_3\\C_3H_3\end{Bmatrix}}_{\text{Boric methide.}} + 6\underbrace{\begin{Bmatrix}C_4H_5\\Zn\end{Bmatrix}}_{\text{Ethylate of zinc.}} O_2.$$

The formation of boric methide under these circumstances proves conclusively that the corresponding ethyl-compound is formed, not by the removal of the whole of the oxygen from boracic ether, but by the actual substitution of the three atoms of oxygen in boracic acid by three atoms of ethyl, whilst boric methide is in like manner produced by the similar substitution of methyl for oxygen,—a kind of substitution which is quite in harmony with the mode of formation of very numerous compounds in the organo-metallic family.

Boric methide exists at ordinary temperatures as a colourless and transparent gas, possessing a peculiar and intolerably pungent odour, irritating the mucous membrane, and provoking a copious flow of tears. Its specific gravity is 1·93137. It retains its gaseous condition when exposed to a cold of —16° C.; but at 10° C., and under a pressure of three atmospheres, it condenses to a colourless, transparent, and very mobile liquid. It is very

sparingly soluble in water, but very soluble in alcohol and in ether. In contact with atmospheric air it takes fire spontaneously, burning with a bright green flame, which is very fuliginous if the volume of the flame be considerable. If the gas issue into the air through a tube $\frac{1}{10}$th of an inch in diameter, the amount of smoke is surprisingly great, two or three cubic inches of gas, when consumed in this way, filling the atmosphere of a capacious room with large comet-like flocks of carbonaceous matter. This curious phenomenon is probably due, in part at least, to the formation of a superficial coating of boracic acid, which envelopes the particles of carbon, and prevents their combustion. Suddenly mixed with atmospheric air or oxygen, boric methide explodes with great violence. In contact with air, both boric methide and the vapour of boric ethide exhibit two distinct kinds of spontaneous combustion. Thus, when these bodies issue very slowly from a glass tube into the air, they burn with a lambent blue flame invisible in daylight, and the temperature of which is so low that a finger may be held in it for some time without much inconvenience. Under these circumstances partial oxidation only takes place, and it is to the products thus formed that the peculiar pungent odour of boric ethide and boric methide is due. When, on the other hand, these bodies issue into the air more rapidly, the lambent blue and nearly cold flame changes to the green and hot flame above-mentioned. I have not examined the spectra of the two differently coloured flames from the same compound, but they doubtless present a widely different appearance, thus affording another instance of the dependence of the spectra of bodies upon temperature,—a phenomenon to which Dr. Tyndall and myself recently called attention in the case of lithium*.

Boric methide is not acted upon by binoxide of nitrogen or by iodine. Solution of bichromate of potash scarcely effects it, but the addition of concentrated sulphuric acid at once determines the reduction of the chromic acid. When boric methide is allowed to bubble through water into chlorine, each bubble burns explosively with a bright flash of light and the separation of carbon. It has no tendency to unite with acids. Concentrated sulphuric acid has no action upon it; when mixed with hydriodic acid gas, it suffers no change; but, on the other hand, it is freely absorbed by solutions of the fixed alkalies, and by ammonia. If a very rapid cur-

* Philosophical Magazine [4], xxii, 472.